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(10) **CANADIAN PATENT**

(54) **PARTICLE AGGLOMERATION**

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U.S.A.

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The instant invention involves an improved method for agglomerating water-wet metalliferous particles by mechanical agitation. In the art of agglomerating particulate solids into larger shapes, it is well known to mechanically agitate water-wet particles to promote the operation of cohesive forces, which produce larger agglomerates of the particulate solids. The mechanical agitation may be produced by rolling or cascading motion as is achieved in balling drums, discs and cones. Another agglomeration method utilizes agitation induced by paddle type agitators, such as in pug mills.

As agglomeration proceeds aggregates in the form of pellets, balls, or granules are formed. As the agglomerates are agitated, e.g. rolled or tumbled, particles are added to their surface as a continuous film. The growth of larger agglomerates is also attributed to coalescence of smaller particles and agglomerates. Sometimes the agglomerates are dusted with finely divided dry particles to minimize sticking problems. When their size is sufficient, the agglomerates are removed from the agitating mechanism for further processing such as induration by heating to low temperatures and sintering at higher temperatures depending upon utilitarian nature of the starting metalliferous materials.

Metalliferous materials which have been successfully agglomerated by agitation include potash fines, aluminum silicate, ferrous chrome fines, zinc oxide, magnesium oxide and the various iron ores.

Regardless of the type of equipment employed and the materials agglomerated, an essential operating parameter of the process is the wetness of the particulate solids. In some instances, as, for example, in the processing of iron ore, the solids are produced in a wet condition and must be dewatered



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prior to agglomeration. In other processes, the solids are initially dry but must be wetted to facilitate agglomeration. Because the process is sensitive to the amount of water either present in the solids to be agglomerated or added thereto, care
5 must be exercised to carefully control this parameter of the process.

Further desiderata of processes for balling, pelletizing and/or granulating finely divided solids include ways and means of increasing equipment throughput and flexibility as to
10 operable particle sizing. A further need of agglomerating processes is reducing the concomitant production of particle fines which must be recycled to the head of the process or discharged as a waste by-product.

It has now been found and the discovery forms the basis
15 for the present invention that the difficulties encountered in agglomerating a particulate solid containing too much water or having too coarse particle size can be substantially eliminated by the addition of a water swellable polymer. The invention therefore concerns an improved process for agglomerating a
20 particulate water wet metalliferous solid by adding a water swellable polymer either prior to or during the agitation step in a proportion to provide for the desired degree of agglomeration. Preferably the agitation is suitable to effect agglomeration into substantially spherical pellets. The process is
25 especially suitable for agglomerating wet ground ores and ore concentrates.

Water swellable cross-linked polymers such as, for example, acrylic polymers and partially hydrolyzed acrylamide polymers have been found particularly useful in the process of
30 the invention and are usually used in a proportion to provide 0.0025 to 0.10 and preferably 0.01 to 0.02 percent of the

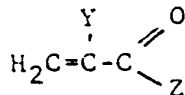
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weight of the moist solid. The preferred polymers have a gel capacity of at least 100. The gel capacity is the number of grams of water absorbed by one gram of the polymer, the free water having been drained away by gravity. Not only is water tolerance increased but the agglomerates are usually found to have improved green strength.

The highly water-swellaable polymers useful herein are the lightly crosslinked analogs of water soluble polymers. Their effectiveness per unit mass will be optimized within a particle size range from about 50 to about 200 mesh, U. S. Standard Screen Series.

Useful water-swellaable polymers can be made by any of several known preparative techniques. For instance, a mono-ethylenically unsaturated monomer feed, of which at least a major proportion is water-soluble, is copolymerized with a small proportion of a polyunsaturated monomer by either mass, solution, suspension or emulsion polymerization methods to provide a lightly crosslinked polymer. To achieve a gel capacity in accordance with the invention, the amount of polyunsaturated crosslinking agent should not exceed about one mole percent of the monomer charge.

Preferred for use in the invention are water-swellaable acrylic polymers. These are copolymers of water-soluble monomers having the formula:



wherein Y is ethyl, methyl or hydrogen, Z is an $-\text{NH}_2$ group, or an $-\text{OM}$ group wherein M is an alkali metal or ammonium moiety. Examples of such monomers are acrylamide, methacrylamide, acrylic acid, sodium acrylate and potassium methacrylate.

One or more of such monomers are copolymerized with a small amount of a crosslinking polyfunctional ethylenically unsaturated monomer. The amount of the crosslinker may vary from 0.005 up to as much as 1 mole percent of the monomer charged to the polymerization system. Preferably, the amount of crosslinker is within the range from 0.05 to 0.7 mole percent, of the monomer charge.

Illustrative of useful polyfunctional monomers are methylenebisacrylamide, N,N-diallylacrylamide, diallylamine, diallylmaleate, ethylene glycol dimethacrylate, divinylbenzene, divinyl ether of diethylene glycol, trivinylbenzene, materials having more than one ethylenically polymerizable double bond.

In addition certain monoethylenically unsaturated, water-soluble monomers, or pre-existing linear, soluble polymers of such monomers, can be lightly crosslinked to prepare water-swellaible polymers by irradiation in aqueous solution with suitable dose of high energy ionizing radiation.

In the practice of the invention, agglomeration of the metalliferous particles can be readily carried out in such equipment as disc or drum pelletizers. Pug mills may also be used for this purpose. In general, the necessary mechanical means subject the particles to agitation in a manner to cause particle agglomeration into balls or pellets.

The essential common feature of agglomeration operations is in the utilization of water to promote the cohesive properties of the particles. This water may be present in the particles (sometimes referred to herein as burden) as a result of prior processing steps, such as grinding and crushing, or may be added to an already dry burden to promote its agglomerating properties. Regardless of whether water is already present in the burden to be agglomerated or is to be applied thereto,

the water swellable polymer is preferably added to the already water-wet particles to be agglomerated. Mixing may be accomplished in a processing step prior to agglomeration of the burden but good results are also achieved by uniformly dusting the small amount of polymer used onto the burden as it is being subjected to agitation to induce agglomeration. When applied prior to agglomeration, the polymer should be mixed with the burden in a manner to achieve uniform distribution. This may be accomplished by application of the polymer intermittently or from many points of application and subjecting the burden to thorough mixing agitation as can be achieved in a pug mill. The polymer may also be introduced as by spraying a slurry thereof within a dispersion facilitating organic liquid, such as diethylene glycol, ethanol or toluene, non-solvents for the polymer.

The dose of swellable polymers is controlled in relation to the amount of water present in, or to be added to, the burden. One of the most important advantages is achieved in the practice of the invention when polymer is employed to cause pelletization or balling of burden that is initially too wet. In such cases enough polymer is added within the range of 0.05 up to 2 parts per 2000 parts by weight of wet burden to induce the desired balling or agglomeration. The lower limit is only significant in that it reflects the approximate onset of significant modification of the burden. The upper limit on the other hand, is important in that a larger amount would interfere with the strength properties of the agglomerates. The green strength properties of agglomerates containing polymer is usually improved thus allowing for more efficient handling usually in drying and sintering operations often employed in the processing of ores.

When employed in the practice of pelletizing with clay, the polymer-clay combination produces an unexpectedly enhanced tolerance for water content, as well as balls or pellets of improved strength properties in the dried and sintered states.

5 When practiced in this manner, the clay is preferably added into the ore particles prior to balling in amount within a range from 0.05 up to 1% by weight on the dry weight of ore particles.

In the following specific embodiments, the invention will be further illustrated in respect of operating techniques.

10 In particular, balling tests were conducted on magnetite concentrates which had been ground to a particle size characterized by 62.7 weight percent passing 325 mesh screen U. S. Standard Screen Series. Particles were further characterized by a surface area of approximately 1600 square centimeters per gram
15 as measured by the Blaine permeability method described at ASTM Specification C204-55 ASTM Vol. 9 (1965) page 207.

Samples of the wet ore concentrate containing 9.5 percent by weight moisture in amount of 2000 grams were mixed thoroughly with incrementally increased small amounts of a
20 highly water-swellable polymer. The particular water-swellable polymer employed was characterized as a lightly crosslinked copolymer of acrylamide and methylenebisacrylamide, which copolymer had been hydrolyzed to the extent that 25 percent of the initially available carboxamide groups were replaced by sodium
25 carboxylate groups. The copolymer was characterized by a gel capacity in distilled water greater than 100 and a particle size of 200 mesh (U. S. Standard Sieve).

The wet particles of magnetite ore were formed into pellets of an approximate diameter of 0.5 inch (12.7 mm) on a
30 laboratory model balling pan. During the balling operation, additional water was added to the ore-polymer mixtures as a

finely atomized spray. Water addition was terminated when it appeared that the balling operation was deteriorating as evidenced by the coalescence of small pellets in clusters which grow uncontrollably to form large botryoids.

In the above manner, several series of experiments were conducted to ascertain the maximum permissible water contents for given concentrations of water-swellable polymer. The moisture content of the agglomerated ore balls was measured by weighing before and after drying at a temperature of 230°F.

(110°C.) for approximately 24 hours.

In a similar series, 10 grams of bentonite was added along with the polymer to demonstrate the conjoint effect of the polymer and clay binder.

The results of the above operations are depicted in Table 1 which shows a decided increase in the maximum possible water content in pelletizable burden treated with varying doses of polymer. Table 2 illustrates the unique interaction of clay and water-swellable polymer in terms of the same parameters.

Further advantages which may be expected from the application of the described water-swellable polymers include less need for close control over the particle size to be bailed. The polymers enable the balling of coarser sizes. Also due to the more rapid growth of the balls, the throughput of the balling equipment is increased.

TABLE 1

<u>Run No.</u>	<u>Grams Polymer</u>	<u>% Water in Green Ball</u>
1	0.0	9.62
2	0.2	10.35
3	0.4	10.52
4	0.6	10.87

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TABLE 2

[With Bentonite]

<u>Run No.</u>	<u>Grams Polymer</u>	<u>Water in Green Ball</u>
5	0.0	9.78
6	0.1	10.57
7	0.2	10.99
8	0.3	11.14
9	0.4	11.25

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In the method for agglomerating finely divided water-wet metalliferous solids by mechanically agitating the wet solids, the improvement which comprises incorporating into the wet solids a highly water-swellable, acrylic polymer characterized by a degree of cross-linking corresponding to that produced by copolymerizing a monoethylenically unsaturated monomer with from 0.05 to 0.7 mole percent of a polyunsaturated monomer and having a gel capacity of at least 100.
2. A method as in Claim 1 wherein the polymer is employed in an amount from about 0.05 to 2 pounds per ton of wet solids.
3. A method as in Claim 1 wherein the metalliferous solids are a ground iron ore and the agitation is of a tumbling nature to induce pelletizing of the wet solids.
4. A method as in Claim 3 wherein the amount of polymer employed is within the range of about 0.05 to 0.4 pound per ton of wet solids.
5. A method as in Claim 1 wherein a finely divided clay is also added to the wet solids in an amount from about 0.05 to 1% based on the dry weight of the ore.
6. The method as in Claim 4 wherein the polymer is a lightly cross-linked copolymer of acrylamide and methylenebisacrylamide, hydrolyzed to the extent that about 25 percent of the initially available carboxamide groups have been replaced by sodium carboxylate groups.



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